

## DESCRIPTION

NANOSTRUCTURE, ELECTRONIC DEVICE AND METHOD OF  
MANUFACTURING THE SAME

5

## TECHNICAL FIELD

The present invention relates a nanostructure formed of a mixture including Al, Si and/or Ge, an electronic device and a method of manufacturing the same. In this specification, (Si, Ge) denotes Si, Ge or a mixture including Si and Ge. More particularly, the present invention relates to a structure in which Al cylinders forming a honeycomb array are orderly formed in a (Si, Ge) matrix region.

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## BACKGROUND ART

In recent years, there has been a growing interest in microstructures of a nanosize applicable to functional materials and functional devices.

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As a method of fabricating such a microstructure, a method may be mentioned in which a microstructure is directly fabricated by a semiconductor processing technique typified by a fine pattern forming technique such as photolithography.

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Apart from the above-described semiconductor processing technique, there is a technique using the phenomenon of self-organization or self-formation of

a material. That is, a novel microstructure is thereby realized on an orderly structure spontaneously formed.

5        There is a possibility that a structure on the order of nanometers as well as those on the order of microns will be easily realized by the technique using the self-organization or self-formation phenomenon. A number of studies have therefore been made on this kind of technique. For example,  
10       Japanese Patent Application Laid-Open No. H10-321834 discloses a method of forming a metallic fine grain aggregate in the form of a wire by using a phenomenon in which metallic fine grains separate in a self-organization manner by their mutual electric or  
15       magnetic action.

      As a method of forming fine orderly holes, anodized alumina film may be mentioned. An anodized alumina film is a porous film having fine holes grown in the film surface perpendicularly from the film  
20       surface (R. C. Furneaux, W. R. Rigby & A. P. Davidson NATURE vol. 337 P147 (1989)). This porous oxide film is characterized by having a unique geometrical structure in which extremely fine holes having a diameter of several nanometers to several hundred  
25       nanometers are arrayed at intervals of several nanometers to several hundred nanometers generally in parallel with each other.

These fine holes have a high aspect ratio and have improved uniformity in the diameter in their cross sections. The diameter and the interval of these fine holes can be controlled to some degree by  
5 adjusting the current and voltage at the time of anodization.

Also, a technique of forming fine holes in a Si substrate surface by anodization of Si is generally known. Ordinarily, in this anodization, a positive  
10 voltage is applied to the substrate in a fluoric acid solution to etch and remove Si, thereby forming fine holes.

While various studies have been made on fine structures as described above, there has been a  
15 demand for a novel microstructure smaller in size and controlled a method of manufacturing such a microstructure.

For instance, the interval between fine holes in anodized alumina film is ordinarily larger than 10  
20 nm, while the fine hole diameter is slightly smaller than 10 nm. It is extremely difficult to fabricate an orderly structure having such a size.

Also, fine holes can easily branch off in anodization of Si and only a restricted substrate can  
25 be used. It is also difficult to obtain orderly fine holes of a nanosize. Also, it is difficult to fill such fine holes with a material such as a metal.

## DISCLOSURE OF THE INVENTION

Therefore, an object of the present invention is to provide a nanostructure and a method of manufacturing the nanostructure, more particularly a method of manufacturing a nanostructure as an ordered structure smaller than a size of 10 nm.

According to an aspect of the present invention, there is provided a nanostructure in the form of a mixture film which comprises a plurality of cylinders comprising Al as a major constituent, and a matrix region surrounding the plurality of cylinders and comprising Si and/or Ge,

wherein the total amount of Si and Ge is contained in a proportion in the range from 20 to 70 atomic % in the mixture film; the cylinders are orderly arrayed; the diameter of the cylinders is in the range from 1 to 30 nm; and the interval between the cylinders is 30 nm and less.

According to another aspect of the present invention, there is provided a method of manufacturing a nanostructure in the form of a mixture film having a plurality of cylinders having a diameter in the range from 1 to 30 nm and an interval of 30 nm and less and comprising Al as a major constituent, and a matrix region surrounding the plurality of cylinders and comprising Si and/or Ge, the method comprising the steps of:

forming an orderly region for growing Al with priority on a substrate, and thereafter

forming the mixture film which has Al and Si and/or Ge and in which the total amount of Si and Ge is contained in a proportion in the range from 20 to 70 atomic %, to fabricate the mixture film.

According to still another aspect of the present invention, there is provided a structure comprised by a first material and a second material, characterized in that a columnar member comprised by the first material is surrounded by a region comprised by the second material, that the second material in the structure is contained in a proportion in the range from 20 to 70 atomic % of the total amount of the first material and the second material, and that the columnar member is placed on a growth starting portion provided in advance.

According to a further aspect of the present invention, there is provided a method of manufacturing a structure, characterized by having a step of preparing a substrate having a growth starting portion, and a step of forming a structure having on the substrate a columnar member comprised by a first material and a region comprised by a second material and surrounding the columnar member, the second material being contained in a proportion in the range from 20 to 70 atomic % of the total amount of the

first material and the second material in the structure.

In the method of manufacturing the Al-(Si, Ge) mixture film nanostructure in accordance with the present invention, the ordered region in which Al is grown or attached with priority in comparison with (Si, Ge) is fabricated on the substrate in advance.

It is assumed that expression (Si, Ge) in the present invention denotes Si, Ge or a mixture of Si and Ge ( $\text{Si}_x\text{Ge}_{1-x}$  ( $0 < x < 1$ )).

Description will be made as to how the present invention was achieved.

The inventors of the present invention came up with findings described below in the course of pursuing the study of microstructures using Al.

That is, the inventors found a case where Al was formed in a columnar structure in a self-formation manner under certain conditions when (Si, Ge) was added at the time of formation of Al film on a substrate.

The inventors also found it possible to selectively grow Al columnar structure in a place where Al could grow easily. The inventors of the present invention earnestly pursued the study on the basis of the above-described findings to achieve the present invention.

Applications of the Al-(Si, Ge) mixture in the

present invention to various basic materials and various devices are conceivable. For instance, applications to various quantum electronic devices including single-electron transistors and single-electron memories. Since Al is a superconductor, applications to superconducting Josephson devices and quantum computing devices are possible if fine superconducting cylinders or small spacings between the cylinders are used.

10           Also, the Al-(Si, Ge) mixture in the present invention can be used as a dry etching or wet etching mask for the purpose of processing a separate substrate or a film on a substrate.

15           Also, a structure in accordance with the present invention is constituted by a first material and a second material and characterized in that a columnar member constituted by the first material is surrounded by a region constituted by the second material, that the second material in the structure is contained in a proportion in the range from 20 to 20 70 atomic % of the total amount of the first material and the second material, and that the columnar member is placed on a growth starting portion provided in advance.

25           A method of manufacturing a structure in accordance with the present invention is characterized by having a step of preparing a

substrate having a growth starting portion, and a step  
of forming a structure having on the substrate a  
columnar member constituted by a first material and a  
region constituted by a second material and  
5 surrounding the columnar member, the second material  
being contained in a proportion in the range from 20  
to 70 atomic % of the total amount of the first  
material and the second material in the structure.  
The growth starting portion is a portion on which at  
10 least the columnar member is formed, and which has a  
convex or projecting shape.

#### BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1A is a perspective view of a  
15 nanostructure in accordance with the present  
invention;

Figure 1B is a top plan view of an example of  
the nanostructure in accordance with the present  
invention;

20 Figures 2A, 2B, and 2C are diagrams showing an  
example of the method of manufacturing the  
nanostructure of the present invention;

Figures 3A and 3B are diagrams showing an  
example of the nanostructure of the present  
25 invention;

Figures 4A, 4B, 4C, and 4D are diagrams showing  
the process of fabricating the nanostructure of the



present invention;

Figures 5A, 5B, and 5C are diagrams showing the process of fabricating the nanostructure of the present invention;

5        Figure 6 is a diagram schematically showing a single-electron memory using an Al-(Si, Ge) mixture body in accordance with the present invention; and

      Figure 7 is a diagram showing the method of fabricating the nanostructure of the present  
10       invention.

#### BEST MODE FOR CARRYING OUT THE INVENTION

An embodiment of the present invention will be described in detail with reference to the drawings.

15       (Construction of Nanostructure)

      Figure 1A is a perspective view of a nanostructure in accordance with the present invention. Figure 1B is a top plan view of a film of the present invention. In Figures 1A and 1B, Al-(Si, Ge) nanostructure is indicated by 11, a matrix region  
20       surrounding cylinders and having (Si, Ge) as a major constituent is indicated by 12, the cylinders having Al as a major constituent are indicated by 13, and a substrate is indicated by 14.

25       In the Al-(Si, Ge) nanostructure 11 in the form of film formed on the substrate 14, the proportion of the total amounts of Si and Ge in the total amount is

in the range from 20 to 70 atomic %, preferably in the range from 25 to 65 atomic %, more preferably in the range from 30 to 60 atomic %. If the proportion of Si + Ge is within the above-described range, Al-  
5 (Si, Ge) mixture film having cylinders 13 distributed in matrix region 12 can be obtained.

The above-described proportion (atomic %) is the value when the amounts of Si, Ge and Al in Al-(Si, Ge) mixture film are quantitatively analyzed, for  
10 example, by an inductively coupled plasma emission analysis method. If a value in wt% is used as a unit, the range from 20 to 70 atomic %, for example, is converted into the range from 20.65 to 70.84 wt% (the conversion is made by assuming that the atomic weight  
15 of Al is 26.982 and the atomic weight of Si is 28.086).

The proportion of the total amounts of Si and Ge in the total amount of Si, Al and Ge is the value expressed by  $(\text{Si} + \text{Ge}) / (\text{Si} + \text{Ge} + \text{Al}) \times 100$  in terms  
20 of molar ratio. That is, it is the proportion of Si + Ge in Si + Ge + Al when Si + Ge + Al is 100 atomic %.

In the composition of cylinders 13, Al is contained as a major constituent and any of other  
25 elements such as Si, Ge, oxygen, argon, nitrogen and hydrogen may also be contained as long as columnar microstructures can be obtained.

In the composition of the (Si, Ge) region surrounding the cylinders, Si and Ge are contained as major constituents and any of other elements such as Al, oxygen, argon, nitrogen and hydrogen may also be  
5 contained as long as the (Si, Ge) region surrounds the columnar microstructures having Al as a major constituent.

The matrix region 12 may be used in an amorphous form or a micro-(poly-)crystalline form.  
10 However, the matrix region 12 in the form of amorphous (Si, Ge) is preferred in terms of insulating property, because the band gap is increased by forming amorphous (Si, Ge) relative to that in the case of crystalline (Si, Ge) to improve  
15 the electrical insulating property of the basic material by which the cylinders are spaced apart from each other.

The mixture body used here represents the matrix region and the cylinders grown in the matrix  
20 region.

The cylinders 13 containing Al are circular or elliptical as seen in a plan view from above the film. Needless to say, the cylinders 13 may have any other shape if the cylinders 13 are suitably distributed in  
25 the matrix 12.

The average diameter of the cylinders in the nanostructure in accordance with the present

invention is in the range from 1 to 30 nm, preferably in the range from 1 to 15 nm, more preferably in the range from 2 to 8 nm. If the cylinders have an elliptical shape or the like, the largest diameter  
5 may be set within the above-described range. The average diameter is, for example, the mean value of lengths derived as major axes in a case where the Al portions observed in an SEM photograph of the actual film surface (in an area of about  $100 \times 100$  nm) is  
10 processed in image processing with a computer, and where the Al portions are assumed to be elliptical.

The average diameter of the cylinders tends to become smaller if the total amount of (Si, Ge) is larger. Also, when the total amount of (Si, Ge) is  
15 fixed, the cylinders become finer if the proportion of Si is higher. Therefore, it is possible to control the diameter of the cylinders by controlling the total amount of (Si, Ge) or by controlling the proportion of Si in a case where a mixture of Si and  
20 Ge is used in the matrix region.

In a nanostructure of a nanometer size (generally in the range from the order of subnanometers to 100 nm), a unique electrical, optical or chemical characteristic may be exhibited  
25 if the size is smaller than a certain characteristic length (mean free path or the like). From this viewpoint, nanostructures are considered to be useful

as a functional material. The nanostructure in accordance with the present invention can also be used variously as a nanostructure if the diameter of the cylinders constituting the mixture body is in the  
5 range from 1 to 30 nm, more particularly 15 nm or smaller.

The interval between the plurality of cylinders 13, i.e., the distance between the centers, is 30 nm or less, preferably 15 nm or less, more preferably 10  
10 nm.

Needless to say, the interval satisfies the condition that cylinders do not contact each other. The interval between the plurality of cylinders 13 can be controlled by providing ordered regions as  
15 cylinder growing points described below.

For instance, a microstructure may be mentioned in which the diameter of the above-described Al cylinder in a columnar structure is 1 to 15 nm, the interval between the Al cylinders is 7 to 30 nm, the  
20 ratio of the height and the diameter, i.e., the aspect ratio, of the Al cylinders is 0.1 to 100000, and the Al cylinders are generally perpendicular to the substrate.

The shape of the cylinders 13 seen along a  
25 substrate cross section may be rectangular as shown in Figure 1A, square, or trapezoidal. The length of the cylinders may be selected in the range from 1 nm

to 100  $\mu\text{m}$ .

In particular, in a case where the diameter of the cylinders is, for example, 1 to 15 nm and the center distance is 10 to 20 nm, the length may be  
5 controlled in the range from 1 nm to several microns. When the length is in the range from several nanometers to several ten nanometers (when the ratio of the length and the diameter is low), the cylinders  
1 act as aluminum quantum dots (zero dimension).  
10 When the length is above this range, the cylinders act as aluminum quantum wires (one dimension).

The above-described cylinders 13 containing aluminum are separated from each other by the matrix  
12 having (Si, Ge) as a major constituent, as shown  
15 in Figure 1B. That is, a plurality of columnar structures are distributed in the (Si, Ge) regions.

It is preferred that the cylinders 13 be orderly formed in a particular direction, as shown in Figure 1A. It is particularly preferred that they  
20 are orderly formed perpendicularly to the substrate, as shown in Figure 1A.

It is preferred that the cylinders 13 be orderly arrayed in a particular form. This is an important point in an application. That is, because  
25 of the orderly structure, the cylinders can be made uniform in size and the controllability of physical properties or the like can be improved. Also,

because of the orderliness, the cylinders are uniformly spaced apart from each other, so that the electron tunnel barriers between the cylinders are uniform.

5           Any particular substrate is not exclusively used as the substrate 14. However, an insulating substrate, such as a quartz glass substrate or a plastic substrate, or a semiconductor substrate, such as a silicon substrate, a germanium substrate, a  
10 gallium arsenide substrate or an indium phosphide substrate, may be used. A flexible substrate (e.g., a polyimide resin or the like) may be used if the mixture film can be formed on the substrate serving as a supporting member. Further, a substrate formed  
15 in such a manner that one or more layers are formed on a supporting substrate may be used.

(Method of Manufacturing Nanostructure)

A method of manufacturing a nanostructure in accordance with the present invention will be  
20 described with reference to Figures 2A to 2C. An example of Al dots will be described as orderly regions for growing Al with priority, i.e., cylinder growing points. In Figures 2A and 2B, the substrate is indicated by 14 and cylinder growing points are  
25 indicated by 21.

A difference in shape, a different material or the like can be used for the cylinder growing points

21 if the cylinder growing points 21 are orderly  
regions for growing Al with priority. According to  
the most effective method, dots having Al as major  
constituents are formed in advance on portions where  
5 the Al cylinders are to be grown.

It is most effective to array the cylinder  
growing points 21 so that the cylinder growing points  
21 correspond precisely with the desired cylinder  
array. If it is difficult to form such growing  
10 points, growing points corresponding only to part of  
the desired cylinder array may be formed. Growing  
points thus formed can be recognized as effective.  
For example, in a case where there is a need to  
obtain a honeycomb cylinder array, a graphite array  
15 shown in Figure 3A and having such a configuration  
that some portions of the honeycomb array are lost  
can be used. As shown in Figure 3B, cylinders 33 are  
formed from starting points corresponding to the  
cylinder growing points 21 as described above, and  
20 cylinders 32 are also grown in places where no  
cylinder growing points 21 are formed. This is due  
to the self-organization of the material. In this  
case, however, there is a possibility of a difference,  
e.g., a slight difference in diameter being  
25 recognized between the cylinders at the growing  
points and the cylinders growing in a self-  
organization manner. It is not necessary that the



array of cylinder growing points 21 be a honeycomb array. A square array or a rectangular array may be used as the array of cylinder growing points 21. In such a case, however, it is difficult to obtain  
5 cylinders having a high aspect ratio.

As a method of fabricating such growth starting points, a method may be used in which portions of Al surface is oxidized by an SPM method and points not oxidized are formed as cylinder growing points 21.  
10 However, a method using nanoimprinting or anodization may be mentioned as a more efficient method. For example, as shown in Figure 4A, Al film 42 is anodized on the substrate and anodization is stopped at a suitable point in time. After anodization,  
15 portions 46 where Al has not been oxidized remain in a graphite array on the substrate surface (Figure 4B). The oxidized anodized film is removed by etching (Figure 4C) to form Al dots 46 in the graphite array on the substrate (Figure 4D). Cylinders are  
20 fabricated on these dots formed as cylinder growing points 21. The cylinders are thereby formed in a honeycomb array. Self-organization also contributes to this formation. It is to be noted here that the density of the cylinders is thrice the density of the  
25 original fine holes in the Al anodized film.

An example of formation of Al-(Si, Ge) mixture film by a magnetron sputtering method which is a film

forming method for forming a substance in a nonequilibrium state will be described as a film forming method in this embodiment.

5 A target as a raw material is obtained by placing an Ge chip or a Si chip 72 on an Al target substrate 71. A plurality of Si chips or Ge chips may be placed separately from each other. However, this placement method is not exclusively used. An Al-(Si, Ge) sintered material prepared by sintering a  
10 predetermined amount a powder of Al and (Si, Ge) may be used as a target material. If such a target is used, a uniform film having reduced variation in film composition can be formed.

15 A method of separately preparing an Al target, an Si target and a Ge target and performing sputtering simultaneously from these targets may alternatively be used.

The total amounts of (Si, Ge) in the film formed is in the range from 20 to 70 atomic % of the  
20 total amount of Al and (Si, Ge), preferably, in the range from 25 to 65 atomic %, more preferably 30 to 60 atomic %.

25 The substrate temperature is 300°C or lower, preferably 200°C or lower. More preferably, the substrate temperature is room temperature or a temperature lower than room temperature. If the total amount of (Si, Ge) is fabricated in such a

temperature range, a nanostructure having cylinders distributed in the (Si, Ge) region can be obtained. In the Al-(Si, Ge) mixture film formed by the film forming method of forming Al-(Si, Ge) in a  
5 nonequilibrium state at a substrate temperature of 300°C or lower, Al and (Si, Ge) form a structure similar to an eutectic structure and Al forms nanocylinders on the order of several nanometers and separates from the (Si, Ge) region in a self-  
10 organization manner. The reason for mentioning similarity to an eutectic is that (Si, Ge) is amorphous in ordinary cases and does not necessarily exist in a crystalline form. For the present invention, the fact that the content of (Si, Ge) in  
15 the composition is larger than that in the case of formation at the eutectic point is also important. If Al-(Si, Ge) film is formed at a specimen temperature not lower than at 200°C, the fabricated Al-(Si, Ge) mixture film starts growing into larger  
20 crystals more stable and having a reduced interfacial area in comparison with a structure formed at a temperature equal to or lower than 200°C, and does not form a nanocylinder on the order of several nanometers.

25       The total amount of (Si, Ge) in the Al-(Si, Ge) mixture body can be controlled, for example, by changing the amount of material of the Si chip or Ge

chip placed on the Al target or by using a target prepared by changing the mixing ratio of Al and the Al-(Si, Ge) powder.

5 In the case of performing film forming in a nonequilibrium state, particularly in the case of sputtering, the pressure in the reactor when argon gas is caused to flow is preferably about 0.2 to 1 Pa. However, the pressure is not particularly limited to this value. Film forming may be performed at any  
10 pressure if argon plasma is formed with stability.

The substrate 14 may be, for example, an insulating substrate, such as a quartz glass substrate or a plastic substrate, a semiconductor substrate, such as a silicon substrate or a germanium  
15 substrate, or any of these substrates on which one or more layers of film are formed. If there is no problem with the formation of aluminum nanocylinders, no particular restrictions are imposed on the selection of the material, thickness, mechanical  
20 strength, etc., of the substrate. The shape of the substrate is not limited to a smooth flat shape. The substrate may have a curved shape or a shape including a certain recess/projection or a step in the surface. However, the shape of the substrate is  
25 not limited to any particular shape if there is no problem with aluminum nanocylinders.

As a film forming method for forming a

substance in a nonequilibrium state, sputtering is preferred. However, any of film forming methods, including evaporation (resistance heating evaporation, electron beam evaporation, etc.) and ion plating, in which a substance is formed in a nonequilibrium state freely selected can be used. Sputtering, evaporation (resistance heating evaporation, electron beam evaporation, etc.), ion plating, etc., are called "PVD".

As a film forming process, a simultaneous film forming process in which Al and (Si, Ge) are simultaneously formed or a stacking film forming process in which layers of several atomic layers of each of Al and (Si, Ge) are stacked may be used.

(Construction of Semiconductor Memory)

Figure 6 is a diagram schematically showing a single-electron transistor using an Al-(Si, Ge) mixture body. Aluminum is formed as quantum dots (islands) as shown in Figure 6 to enable control of electrical characteristics of a channel portion by the influence of electric charge accumulated on the quantum dots. Because electric charge can be accumulated on the quantum dots for a long time, a nonvolatile memory in which information does not disappear even after turning off of power can be formed. In the figure, a substrate is indicated by 61, an insulating material (e.g., silicon oxide) by

62, an Al-(Si, Ge) mixture body by 63, a drain by 64, a gate insulator by 65, a gate electrode by 66, and a source by 67.

5 The single-electron transistor shown herein is described, for example, in "Nanotechnology-no-subete (all about nanotechnology)" (Kogyo Chosakai Publishing Co., Ltd.) pp. 114-117.

10 By applying the Al-(Si, Ge) structure as described above, a single-electron memory using a quantum effect, a single-electron transistor using the same principle, or the like can be put to use.

A Josephson device or the like, not illustrated, can be fabricated by using the superconductor characteristics of Al.

15 This embodiment can be grasped as an "electronic device having the above-described nanostructure on a semiconductor substrate with an insulating film interposed therebetween, and having a control electrode on the nanostructure with an  
20 insulating film interposed therebetween".

The present invention enables an aluminum nanocylinder to be applied in various forms such as a quantum dot and a quantum wire, and remarkably extend the range of its application. The structure in the  
25 present invention can be used in a single state as a functional material and can also be used as a basic material or a mold for a further novel nanostructure.

(Examples)

Examples of the present invention will be described with reference to the drawings.

(Example 1)

5           A nanostructure of the present invention and a method of manufacturing the nanostructure will be described with reference to Figures 4A to 4D and Figures 5A to 5C.

10           In Figures 4A to 4D and Figures 5A to 5C, a substrate is indicated by 41, an Al film by 42, a starting point in anodization by 43, an anodized film by 44, a pore by 45, a residual Al portion by 46, a cylinder growing point by 51, an Al-Si mixture film by 52, a Si matrix region by 53, a cylinder the  
15           forming of which starts from the cylinder growing point 51 by 54, and a cylinder formed by self-organization of a material by 55.

<Al Film>

20           Al film 42 is formed to 30 nm in thickness on Si substrate 41 by using RF magnetron sputtering. Small recesses in a honeycomb array are then formed at intervals of about 15 nm in the surface of Al film 42 by using an FIB (focused ion beam) method, as shown in Figure 4A. The recesses function as  
25           starting points 43 for fine holes in anodization.

<Anodization>

Al film 42 is anodized from the surface.

Anodization is performed by using a 5 mol/l sulfuric acid solution and an anodization voltage of 6 V.

Anodization is stopped when the anodization current decreases slightly. By anodization, the Al film is oxidized to the substrate surface as shown in Figure 4B. While oxidation proceeds to substrate surface at the bottom of each fine hole, residual Al portions 46 not anodized are formed in bottoms of portions among the fine holes.

#### 10 <Etching>

After anodization, etching of the oxide layer is performed by immersing the specimen in a chromic acid-phosphoric acid mixture solution. The anodized alumina film is molten by this etching to expose the residual Al portions 46 on the substrate, as shown in Figure 4C. The residual Al portions 46 have such a structure as to be raised at tripled points among the fine holes. Also, the residual Al portions 46 are in a graphite array, as shown in Figure 4D. As a result of this process step, the interval between the apexes of the residual Al portions 46 is shorter by about 60% than the interval between the fine holes in the alumina film.

#### <AlSi Film Forming>

25 Inverse sputtering is performed in a sputtering apparatus to remove the Al oxide formed on the surface of the residual Al portions 46 before AlSi



film forming. The residual Al portions 46 are thereby reduced to form cylinder growing points 51 in such a state that Al is exposed on the surface, as shown in Figure 5A.

5        AlSi mixture film 52 is then formed from an Al-Si mixture target. In the composition of the Al-Si mixture target used, the mixing ratio is Al 60 : Si 40. The obtained film has substantially the same composition. AlSi mixture film is formed to about  
10    200 nm. As sputtering conditions, an Ar flow rate of 50 sccm, a discharge pressure of 0.7 Pa, and input power of 300 W were set by using an RF power supply. The substrate temperature was set to room temperature.

      As a result, Si matrix 53 having amorphous Si  
15    as a major constituent is grown in the AlSi mixture film 52, and cylinders 54 and 55 grown perpendicularly to the substrate and having Al as a major constituent are formed in Si matrix 53, as shown in Figures 5B and 5C. The cylinders 54 are  
20    grown from the cylinder growing points 51, while the cylinders 55 are not grown from the cylinder growing points 51 but grown in a self-organization manner. Figure 5C is a cross-sectional view taken along line 5C-5C of Figure 5B.

25        The average diameter of the cylinders was about 5 nm, and the average interval between the cylinders was about 8 nm.

A target formed by placing an Si chip on an Al target may be used in place of the mixture target if the desired composition ratio is set.

RF sputtering was used as sputtering in this example, but it is not exclusively used. ECR sputtering, DC sputtering and ion beam sputtering may be used. The sputtering conditions depend on the apparatus and are not limited to those described above.

#### 10 (Comparative Examples)

With respect to a comparative specimen A, only AlSi film forming conditions were changed. A mixture target having a mixing ratio of Al 85 : Si 15 in its composition was used. As sputtering conditions, an Ar flow rate of 50 sccm, a discharge pressure of 0.7 Pa, and input power of 300 W were set by using the RF power supply. The substrate temperature was set to room temperature. The specimen A was observed through an FE-SEM (field-emission scanning electron microscope). In the configuration of the surface as seen from above the substrate, which is a direction perpendicular to the substrate, the Al portions were not circular and had such a structure as to connect continuously one to another. That is, the structure was different from the microstructure in which Al cylinders are distributed in the Si region. The size (length) of the Al portions largely exceeded 20 nm.

By observing a cross section through the FE-SEM, it was found that the Al portions did not have such a width as to be columnar but formed a large mass exceeding several ten nanometers.

5           For a specimen on a glass substrate as comparative specimen B, a mixture target having a mixing ratio of Al 23 : Si 75 in its composition was used. A mixture film of about 200 nm having almost the same composition ratio as the target composition  
10           was formed to about 200 nm. As sputtering conditions, an Ar flow rate of 50 sccm, a discharge pressure of 0.7 Pa, and input power of 300 W were set by using the RF power supply. The substrate temperature was set to room temperature. The specimen B was observed  
15           through the FE-SEM. In the specimen surface as seen from above the substrate, which is a direction perpendicular to the substrate, no Al portions were recognized. Even by observation of a cross section through the FE-SEM, the clear Al portions were not  
20           observed.

          Specimens in accordance with the above-described comparative examples were made by using a Si-Ge mixture composition or only Ge, and the results were the same. It is possible to form Al  
25           nanocylinders in (Si, Ge) by adjusting the content of Si and Ge to a value within at least the range from 20 to 70 atomic % of the total amount of Al, Si and

Ge. It is also possible to fabricate an Al wire having an improved linearity by performing this adjustment.

As a specimen C, a mixture film of about 200 nm was formed on a Si substrate by using a target having a mixing ratio of Al 60 : Si 40 in its composition. The substrate temperature was set to 220°C. The comparative specimen C was observed through the FE-SEM. In the specimen surface as seen from above the substrate, which is a direction perpendicular to the substrate, no circular or elliptical aluminum portions were recognized. That is, no Al nanocylinders were recognized. That is, it is thought that when the substrate temperature is excessively high, the material changes into a more stable state and therefore any film growth for forming Al nanocylinders as shown in Figures 1A and 1B or Figures 3A or 3B is not effected. (Example 2)

Nanostructures were fabricated in the same manner as in Example 1 except these nanostructures were fabricated so as to have Si contents in the Al-Si composition ratio of every 5% from 20 to 70%.

By observing the specimens through the FE-SEM, it was found that when the Si content was 25% and lower, the diameter of Al cylinders was about 10 nm and the spacing between the cylinders was excessively

small in some places. When the Si content was 60% and higher, Al cylinders were grown at the cylinder growing points but were not fully grown at some of the points. Also, cylinders 55 considered to be  
5 formed by the self-organization process had many defects.

Thus, cylinders are formed to some extent when the Si content is in the range of 20 to 70% but it is effective for forming the desired cylinders to set  
10 the Si content in the range from 30 to 60%.  
(Example 3)

Nanostructures were fabricated in the same manner as in Example 1 except the interval between cylinder growing points was increased to about 20 nm,  
15 Ge was added to Si in the Al-Si composition ratio, and the Al content was set to 60%, and the ratio  $\text{Ge}/(\text{Si} + \text{Ge})$  of every 20% from 0 to 100%.

By observing the specimens through the FE-SEM, it was found that the diameter of Al cylinders was  
20 increased to about 20 nm as the Ge content was increased and some of the cylinders have a diameter close to 30 nm.

The matrix was amorphous even in the case where Ge was used.

25 Thus, it was found that the Al cylinders were formed even when Ge was added, and that it was advantageous to increase the Ge content in the case

of need to form cylinders of a comparatively large size and it was advantageous to increase the Si content in the case of need to fabricate comparatively small cylinders.

5

#### INDUSTRIAL APPLICABILITY

As described above, the present invention makes it possible to provide a microstructure in which cylinders on the order of nanometers having aluminum as a major constituent are orderly distributed in a (Si, Ge) matrix, and a method of manufacturing the microstructure.

This nanostructure enables a more controllable electronic device on the order of nanometers or the like to be fabricated.

15

## CLAIMS

1. A nanostructure in the form of a mixture film which comprises a plurality of cylinders comprising Al as a major constituent, and a matrix  
5 region surrounding the plurality of cylinders and comprising Si and/or Ge,

wherein the total amount of Si and Ge is contained in a proportion in the range from 20 to 70 atomic % in the mixture film; the cylinders are  
10 orderly arrayed; the diameter of the cylinders is in the range from 1 to 30 nm; and the interval between the cylinders is 30 nm and less.

2. The nanostructure according to claim 1, wherein the cylinders are orderly arrayed in a  
15 honeycomb array.

3. The nanostructure according to claim 1, wherein the proportion of the total amount of Si and Ge in the mixture film is in the range from 25 to 65 atomic %.

20 4. The nanostructure according to claim 3, wherein the proportion of the total amount of Si and Ge in the mixture film is in the range from 30 to 60 atomic %.

25 5. The nanostructure according to claim 1, wherein the average diameter of the cylinders is in the range from 2 to 8 nm.

6. The nanostructure according to claim 1,

wherein the interval between the cylinders is 10 nm or smaller.

7. The nanostructure according to claim 1, wherein the matrix region is comprised of amorphous Si and/or amorphous Ge.

8. The nanostructure according to claim 7, wherein the matrix region is amorphous Si.

9. The nanostructure according to claim 1, wherein the matrix region is comprised of amorphous Si and amorphous Ge.

10. The nanostructure according to claim 1, wherein the mixture film is formed on a substrate.

11. An electronic device according to claim 10, comprising wiring on part of the substrate.

12. A method of manufacturing a nanostructure in the form of a mixture film having a plurality of cylinders having a diameter in the range from 1 to 30 nm and an interval of 30 nm and less and comprising Al as a major constituent, and a matrix region surrounding the plurality of cylinders and comprising Si and/or Ge, the method comprising the steps of:

forming an ordered region for growing Al with priority on a substrate, and thereafter

forming the mixture film which has Al and Si and/or Ge and in which the total amount of Si and Ge is contained in a proportion in the range from 20 to 70 atomic %, to fabricate the mixture film.



13. The method of manufacturing a nanostructure according to claim 12, wherein the ordered region is a region having a honeycomb array or a pattern corresponding to part of the honeycomb array.

5           14. The method of manufacturing a nanostructure according to claim 13,

          wherein the honeycomb array or the partial region of the honeycomb array is a graphite array.

10           15. The method of manufacturing a nanostructure according to claim 12, wherein the ordered region for forming Al with priority includes a projection having Al as a major constituent.

15           16. The method of manufacturing a nanostructure according to claim 15, wherein the projection having Al as a major constituent is fabricated by anodization of a film having Al as a major constituent and etching of anodized Al film.

20           17. The method of manufacturing a nanostructure according to claim 12, wherein the method of forming the mixture film is a film forming method of forming a substance in a nonequilibrium state.

25           18. The method of manufacturing a nanostructure according to claim 17, wherein the film forming method of forming a substance in a nonequilibrium state is sputtering.

          19. The method of manufacturing a nanostructure according to claim 17, wherein the substrate

temperature in film forming of forming a substance in a nonequilibrium state is 200°C or lower.

20. The method of manufacturing a nanostructure according to claim 12, wherein the total amount of Si and Ge is a proportion in the range from 25 to 65 atomic %.

21. The method of manufacturing a nanostructure according to claim 12, wherein the total amount of Si and Ge is a proportion in the range from 30 to 60 atomic %.

22. The method of manufacturing a nanostructure according to claim 12, wherein the matrix region is Si.

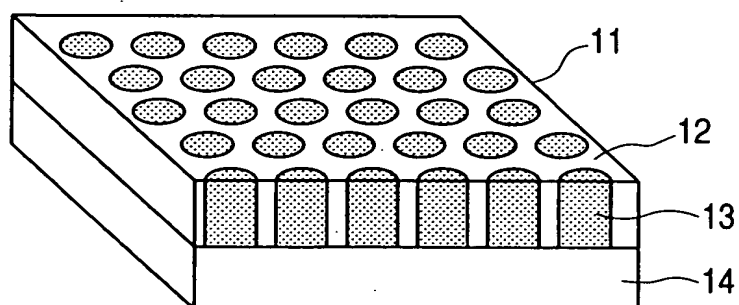
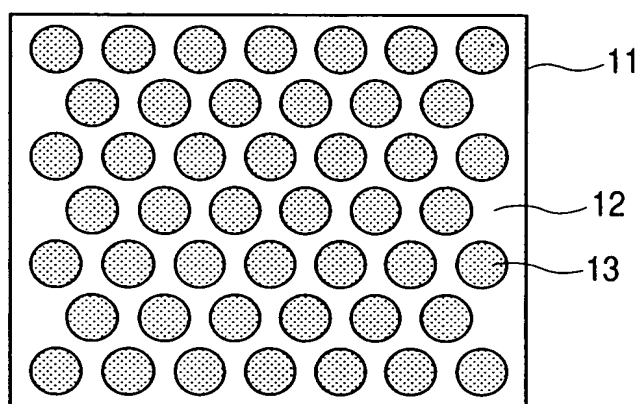
23. A structure comprised by a first material and a second material, characterized in that a columnar member comprised by the first material is surrounded by a region comprised by the second material, that the second material in the structure is contained in a proportion in the range from 20 to 70 atomic % of the total amount of the first material and the second material, and that the columnar member is placed on a growth starting portion provided in advance.

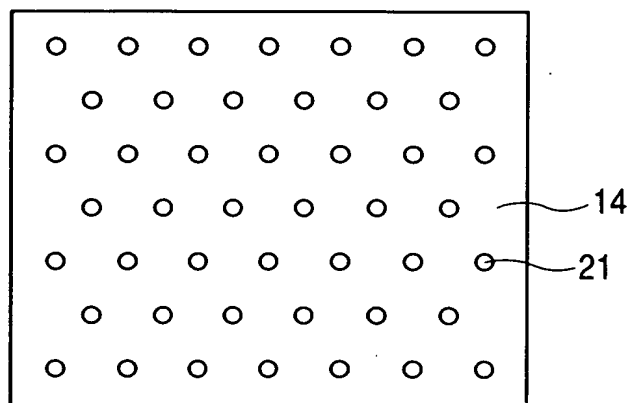
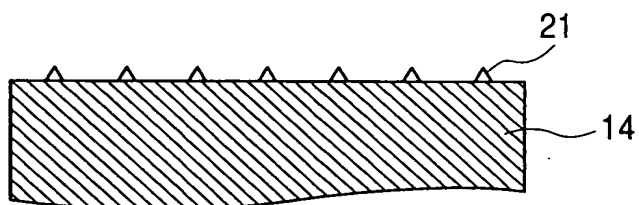
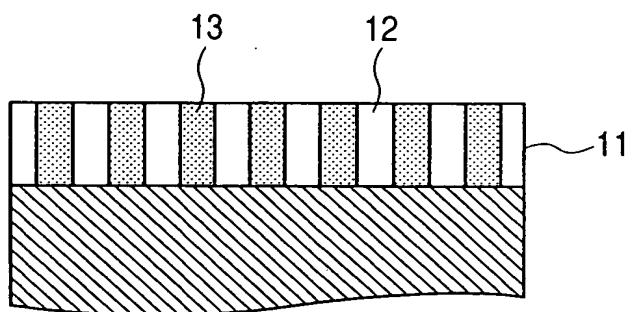
24. A method of manufacturing a structure, characterized by having a step of preparing a substrate having a growth stating portion, and a step of forming a structure having on the substrate a

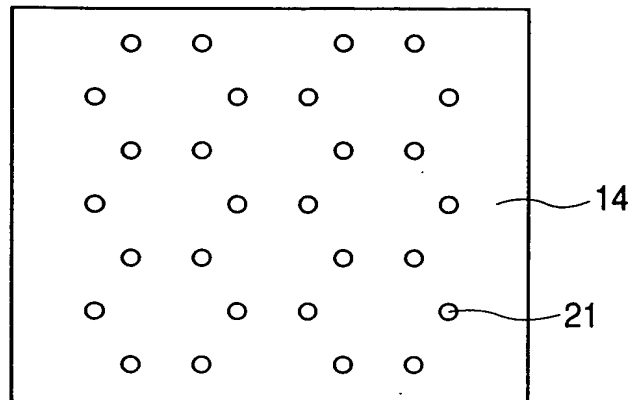
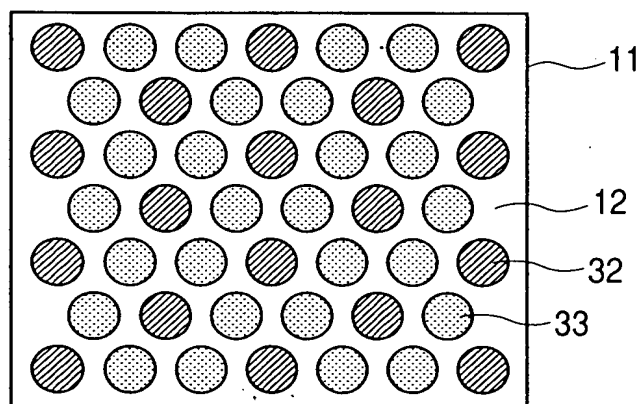
columnar member comprised by a first material and a region comprised by a second material and surrounding the columnar member, the second material being contained in a proportion in the range from 20 to 70 atomic % of the total amount of the first material and the second material in the structure.

## ABSTRACT

Cylinders having Al as a major constituent are orderly arrayed in an (Si, Ge) matrix. In a nanostructure in the form of a mixture film having a plurality of cylinders having Al as a major  
5 constituent, and a matrix region surrounding the plurality of cylinders and having Si and/or Ge as a major constituent, the total amount of Si and Ge is contained in a proportion in the range from 20 to 70  
10 atomic % in the mixture film, the cylinders are orderly arrayed, the diameter of the cylinders is in the range from 1 to 30 nm, and the interval between the cylinders is 30 nm or smaller.

*FIG. 1A**FIG. 1B*

*FIG. 2A**FIG. 2B**FIG. 2C*

*FIG. 3A**FIG. 3B*

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FIG. 4A

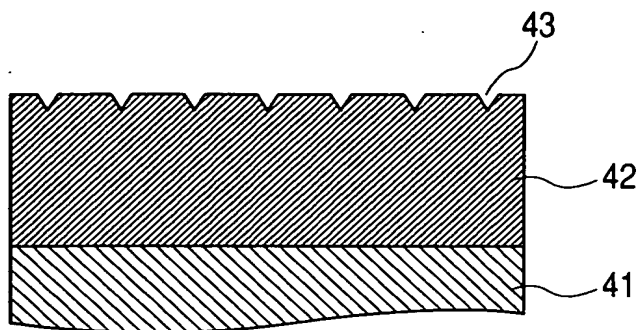


FIG. 4B

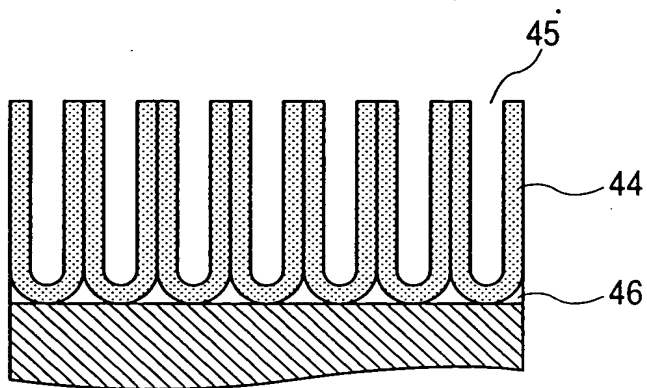


FIG. 4C

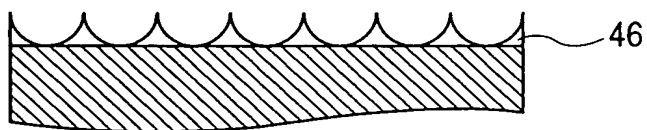
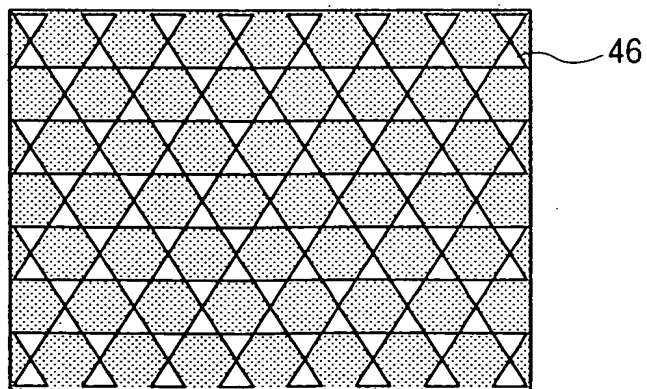


FIG. 4D





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FIG. 5A

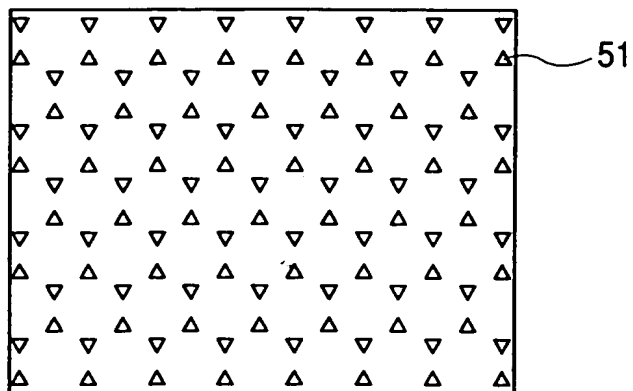


FIG. 5B

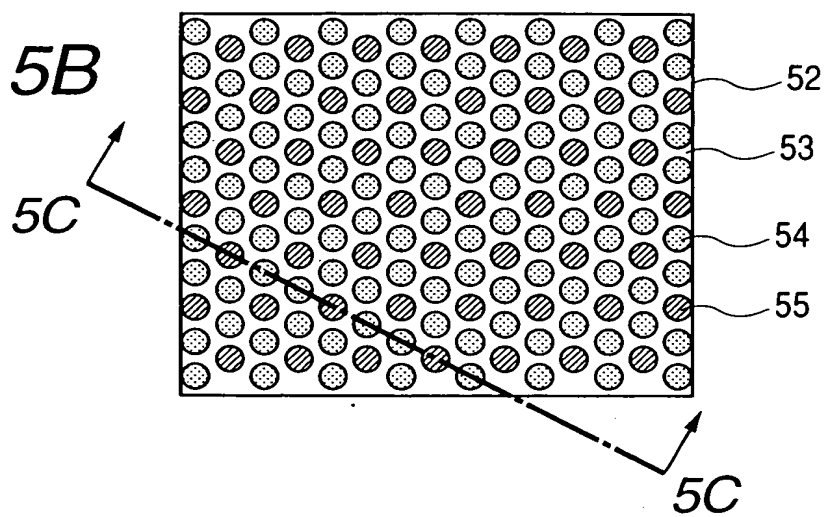
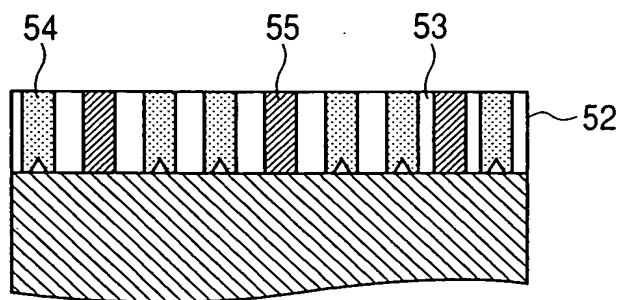


FIG. 5C



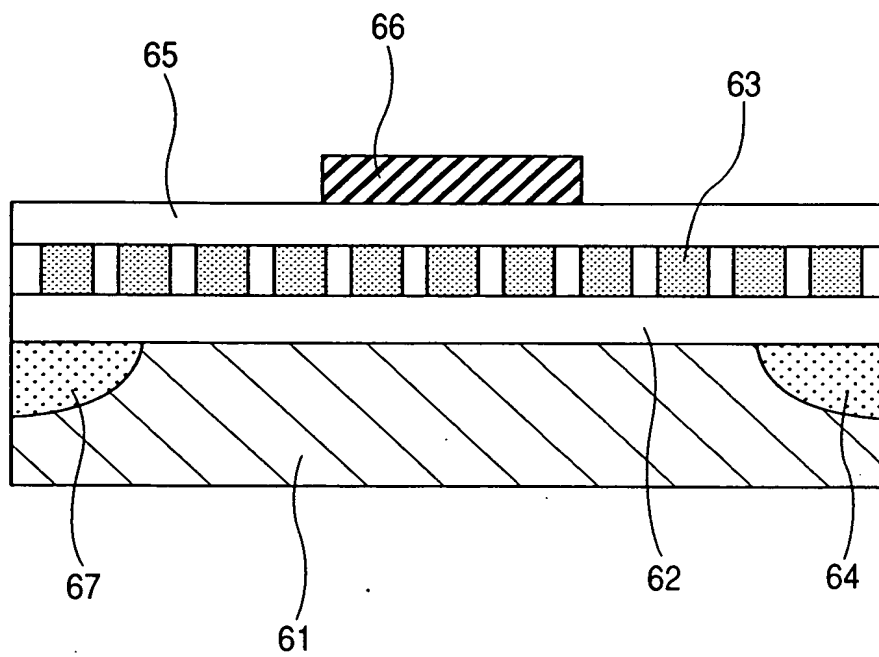
*FIG. 6*

FIG. 7

